

Final Report: AOARD-054036

Title:

Simulation Studies of a Four Component Model of Zr-based Bulk Metallic Glass

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OBJECTIVES

The objective stated in the application was to carry out simulation studies on the 5 component Vitreloy-1 metallic glass. This was to include the characterisation of interaction potentials and the running of preliminary simulation calculations. One specific goal was to compare the outcomes of these calculations with the prediction of a crystal-based structural approximation to the amorphous state recently proposed by Miracle. The project was originally designed to cover the developmental stages of a more extended study of an important glass forming system. Soon after the start of the grant, it became uncertain whether support could be ensured for this extended plan. Furthermore, we realised that a key feature of the project – the examination of the Miracle structural approximation to the amorphous alloy – could be effectively treated within the period of the grant using a variety of hard sphere packing protocols. As a result of these considerations, we modified the objectives to the following.

The objectives of the work reported below was to a) explore the properties and stability of the crystalline approximat for amorphous alloys proposed by Dr Miracle using binary and ternary hard sphere mixtures, b) to clarify the compositional bounds of chemical order in amorphous packings, and c) to establish the utility of hard sphere packings as structural representations of more realistic models of metallic glasses.

ACTIVITIES

The following activities have taken place as part of this project.

Report Documentation Page			<i>Form Approved OMB No. 0704-0188</i>	
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1. REPORT DATE 18 OCT 2007	2. REPORT TYPE Final	3. DATES COVERED 12-04-2005 to 24-01-2007		
4. TITLE AND SUBTITLE Simulation Studies of Zr-based Bulk Metallic Glass			5a. CONTRACT NUMBER FA520905P0274	5b. GRANT NUMBER
			5c. PROGRAM ELEMENT NUMBER	5d. PROJECT NUMBER
			5e. TASK NUMBER	5f. WORK UNIT NUMBER
6. AUTHOR(S) Peter Harrowell			8. PERFORMING ORGANIZATION REPORT NUMBER N/A	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Sydney, School of Chemistry, University of Sydney, Sydney 2006, Australia, AU, 2006			10. SPONSOR/MONITOR'S ACRONYM(S) AOARD	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AOARD, UNIT 45002, APO, AP, 96337-5002			11. SPONSOR/MONITOR'S REPORT NUMBER(S) AOARD-054036	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited				
13. SUPPLEMENTARY NOTES				
14. ABSTRACT The objective of the work was to carry out simulation studies on the 5 component Vitreloy-1 metallic glass. This was to include the characterization of interaction potentials and the running of preliminary simulation calculations. One specific goal was to compare the outcomes of these calculations with the prediction of a crystal-based structural approximation to the amorphous state recently proposed by Miracle. To this end, a computational characterization of the Miracle periodic approximate (MPA) for binary and ternary mixtures of hard spheres was performed. A comparison of the MPA with a chemically ordered amorphous packing indicated that the MPA is successfully describing important features of the local structure of the amorphous state. Details of the study is presented in result section of the report.				
15. SUBJECT TERMS Materials, nanomaterials, Modelling & Simulation				
16. SECURITY CLASSIFICATION OF: a. REPORT unclassified			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 13
b. ABSTRACT unclassified			c. THIS PAGE unclassified	19a. NAME OF RESPONSIBLE PERSON

- 1) Prof. Harrowell and Dr. Fernández visited the Wright Laboratories in Dayton, Ohio during Feb 7-11, 2005. This visit included extensive discussions with Dr Miracle on the proposed research, a seminar presented by Prof. Harrowell on recent research in modeling dynamics in amorphous alloys, discussions with members of Dr Miracle's group and a visit to Dr Miracle's lab.
- 2) Funds from the grant were used to employ two research assistants, A.N.Alcaraz and R.S.Duhau from CNEA in Buenos Aires from April 1, 2005 to January 31, 2006. These workers performed the bulk of the calculations described below under the supervision of Dr. Fernández.
- 3) On Dec. 2, 2004, Dr Miracle visited the University of Sydney where he presented a talk on modeling the structure of metallic glasses and discussed the project with Prof. Harrowell.

OUTCOMES

1) Computational characterisation of the Miracle periodic approximate (MPA) for binary and ternary mixtures of hard spheres.

1.1) Algorithm Development. The algorithm used is a modification of one described by Clarke and Wiley [Phys.Rev.B 35, 7350 (1987)] which efficiently generates the closest packing configuration in a system of hard spheres. The innovation in this project was to use as starting configurations an array of solute particles (labelled B, and C, in the case of the ternary mixture) on the sites of a crystalline FCC lattice (B particles) and in the octahedral interstitial sites (C particles) in accord with the Miracle periodic approximate (MPA). The lattice was then expanded to accommodate the random insertion of the solvent (A particles). This procedure ensured that solute-solute contact was avoided initially and thus introduced chemical order into the hard sphere system for which there is no such 'natural' inclination. The relaxation of the resulting configuration resulted in the configurations that we refer to here as "constrained". "Unconstrained" configurations were generated by placing particles in random positions in the simulation cell and maximising the density. The packing fraction η of a system with n components and no overlap ($S=0$) is defined as:

$$\eta = \frac{4\pi}{3} \frac{\sum_{i=1}^n N_i R_i^3}{V}$$

where $V=n \times n \times n \times a^3$ is the volume of the simulation cell.

As a validation of the algorithm, a system of hard spheres of equal size was studied. The maximum packing fraction obtained by our algorithm was 0.641, in good agreement with the accepted value for random close packed spheres of 0.64.

1.2) Properties of the MPA. Two binary ($R_B/R_A=0.80$ and $1,12$) and one ternary ($R_B/R_A=0.80$ and $R_C/R_A=0.62$) systems with various compositions were studied. The radius ratio chosen correspond to definite theoretical coordination numbers: $R_B/R_A=0.62$ corresponds to $Z_{BA}=8$, $R_B/R_A=0.80$ to $Z_{BA}=10$, and $R_B/R_A=1.12$ to $Z_{BA}=15$, where Z_{ij} is the number of spheres of type j around a sphere of type i .

The configurations chosen for these studies were those with the highest η values obtained during each relaxation process. Pair correlation functions $g_{ij}(r)$ and coordination numbers Z_{ij} were calculated. The number of i - j bonds in any system can be written as $N_i Z_{ij} = N_j Z_{ji}$, then it is possible to write $Z_{ji} = Z_{ij} X_j / X_i$, where $X_i = N_i / \sum N_i$ is the fraction of the component i . Therefore, there will be only three independent coordination numbers (Z_{AA} , Z_{BA} and Z_{BB}) for a binary system and six (Z_{AA} , Z_{BA} , Z_{BB} , Z_{CA} , Z_{CB} and Z_{CC}) for a ternary.

For calculating Z_{ij} it is necessary to define the maximum distance r_{ij} for which two spheres i and j are considered nearest neighbours. This distance is defined as the one at which the function $g_{ij}(r)$ has its first minimum. The r_{ij} distances found are shown in Table I. They depend on the size ratio but are independent on the system composition.

binary system			
R_B/R_A	r_{AA}	r_{AB}	r_{BB}
0.8	2.7	2.5	2.25
1.12	2.7	2.9	2.7/3.0*

ternary system						
$R_B/R_A; R_C/R_A$	r_{AA}	r_{AB}	r_{AC}	r_{BB}	r_{BC}	r_{CC}
0.8;0.62	2.7	2.5	2.3	2.2	2.0	1.7

*value corresponding to the unconstrained case

Table I: First minimum distances r_{ij} (in units of R_A) for the functions $g_{ij}(r)$ in the studied cases.

The sizes of the systems studied ranged from 1.0×10^3 to 6.8×10^3 spheres. Most of them have $4 \times 5 \times 5 \times 5 = 500$ spheres of type B and a variable number of spheres of type A, according to the value of the chosen fcc lattice parameter a . The composition range was $X_B \sim 0.07$ - 0.50 .

Crystalline order in the solvents was found around two composition values, 0.125 and 0.25. The crystal structures were identified as Ca_7Ge ($X_B=0.125$) and AlFe_3 ($X_B=0.25$). The presence of these fully ordered structures clearly represents a complication in the use of the MCA in describing amorphous states.

The packing fraction η for both systems with either size ratio is plotted as function of X_B in Figure 1. Except for the crystal compositions, there are no important differences between constrained and unconstrained systems. Figure 2 shows the coordination numbers Z_{ij} as a function of X_B for both systems. The peaks and cusps at $X_B=0.125$ and 0.25 correspond to the formation of crystal structures. It can be seen that the average coordination numbers Z_{AA} and Z_{BA} are similar to the corresponding theoretical coordination numbers in the low composition region ($Z_{AA} \approx 12$, $Z_{BA} \approx 10$ for $R_B/R_A=0.8$ and $Z_{BA} \approx 14-15$ for $R_B/R_A=1.12$). It is interesting to mention that cluster sizes distributions

were rather narrow in most of the systems. For example, around 50% of the B spheres have $Z_{BA}=10$, while 20% have $Z_{BA}=9$ and another 20% have $Z_{BA}=11$ for the constrained systems with $R_B/R_A=0.8$ at $X_B < 0.30$.

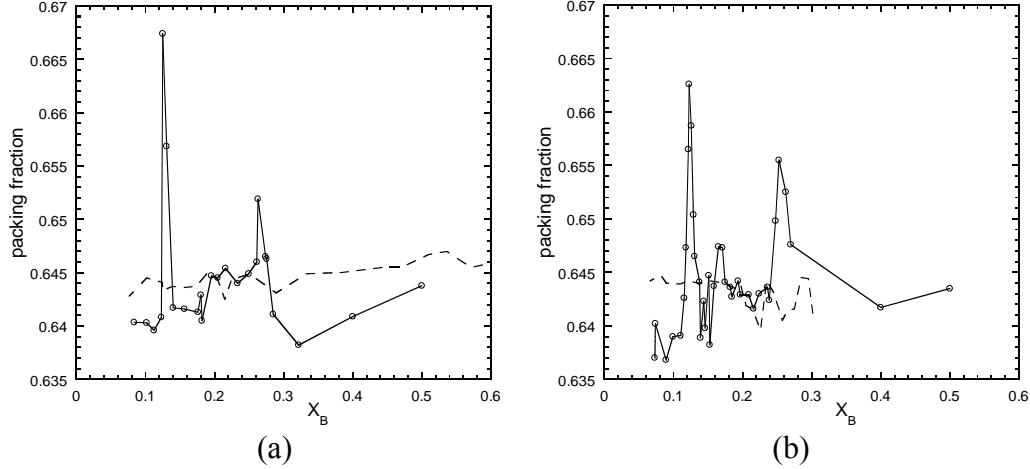


Figure 1: Packing fractions η for the binary systems studied: a) $R_B/R_A=0.80$, b) $R_B/R_A=1.12$. The full line and symbols (dashed line) correspond to the constrained (unconstrained) system.

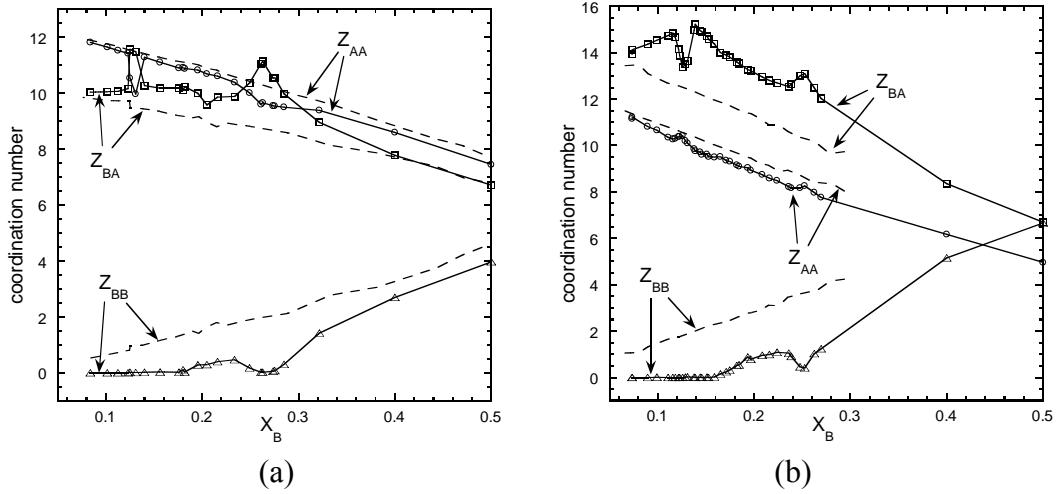


Figure 2: Coordination numbers Z_{ij} for the binary systems studied: a) $R_B/R_A=0.80$, b) $R_B/R_A=1.12$. The full line and symbols (dashed line) correspond to the constrained (unconstrained) system.

1.3) Stability of the MPA. Although in its original form the model considers that the distortions involved destroy the long range order, the structure analysis is much easier when the B spheres are assumed to occupy fcc lattice positions. To quantify the magnitude of the distortions, the displacement suffered by the B spheres from the initial perfect fcc lattice were calculated. Figure 3 shows the square displacement distributions for the whole range of compositions for both binary systems studied and Figure 4 the corresponding mean square displacement. Again, the cusps and peaks are due to the formation of crystal structures. In general, it can be seen that the displacements from the ideal fcc lattice are of the order of R_A or smaller, except for compositions larger than

around $X_B=0.3$ where the number of B-B contacts increases rapidly and the subjacent fcc lattice completely falls apart.

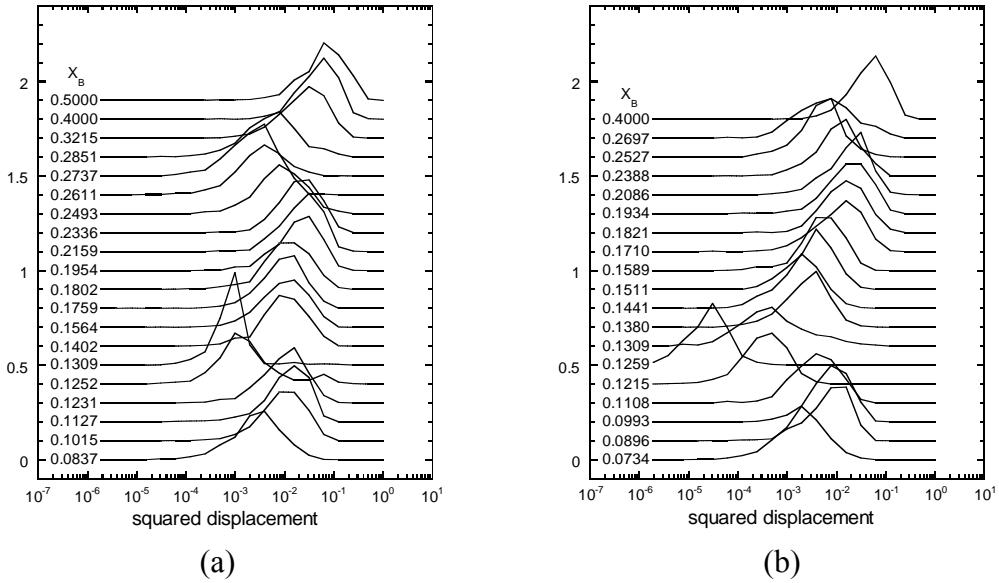


Figure 3: Squared displacement distribution of B spheres with respect to their ideal fcc positions for the binary hard spheres systems studied as a function of the composition X_B : a) $R_B/R_A=0.8$, b) $R_B/R_A=1.12$. The squared displacements are given in units of the fcc lattice parameter a .

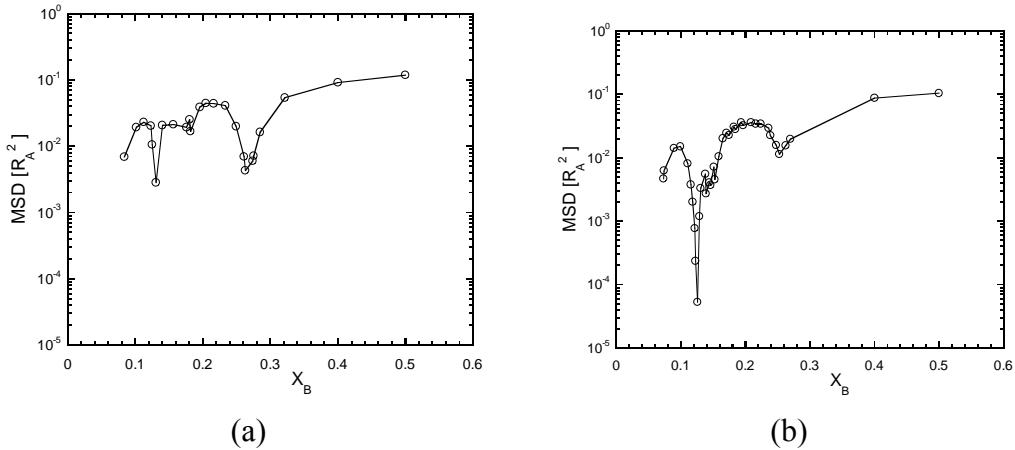


Figure 4: Mean squared displacements (MSD) for the binary hard spheres systems studied as a function of the composition X_B : a) $R_B/R_A=0.8$, b) $R_B/R_A=1.12$. The MSD is given in units of the radius of the fcc lattice parameter a .

A number of valuable observations relating to these results can be made.

i) We find that the original solute ordering is retained upon density maximisation up to $X_B = 0.19$ for $R = 0.8$ and $R = 1.12$ (see Figs 3 and 4). Over the same composition range these systems have a density within 1% of the random packing case and of configuration numbers Z_{AA} very close to that observed in the random packing case. These results

support the basic contention of the MCA that one can produce a very reasonable packing result while retaining a crystalline organisation of the solutes.

ii) The presence of crystalline phases is a difficulty for the MCA in that they create compositional ‘blindspots’ where we cannot extract any useful information about amorphous packing. Here the use of a random close packed structure rather than fcc for the alpha solutes would be of benefit.

1.4) The MPA for a Ternary Alloy. The total number of spheres in these systems range from 1.7×10^3 to 8.7×10^3 . The number of B and C spheres were the same (i.e., $X_B=X_C$), 500 of each type. Therefore, the composition range was $X_B \sim 0.06-0.25$.

As in the binary system case, there are two compositions for which crystal formation was found. For $X_B=0.25$, the structure formed corresponds to AlMnCu_2 ($\text{L}2_1$): Al and Mn

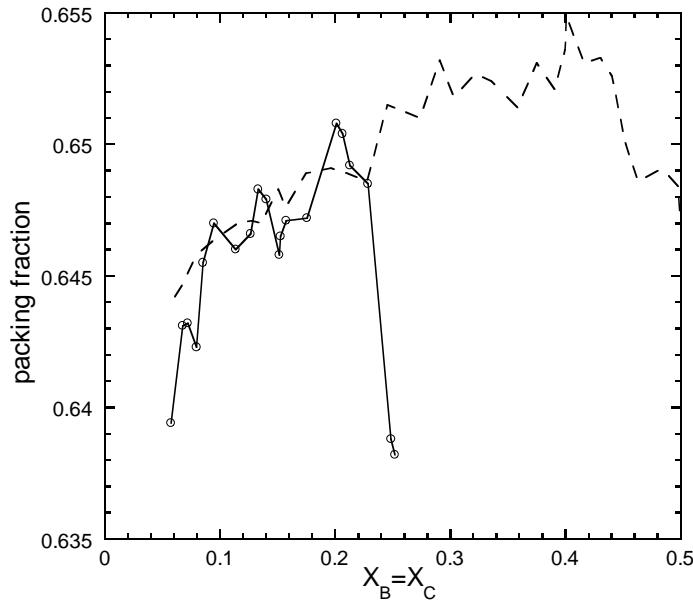


Figure 5: Packing fraction η for the ternary system studied, $R_B/R_A=0.80$ and $R_C/R_A=0.62$. The full line and symbols (dashed line) correspond to the constrained (unconstrained) system.

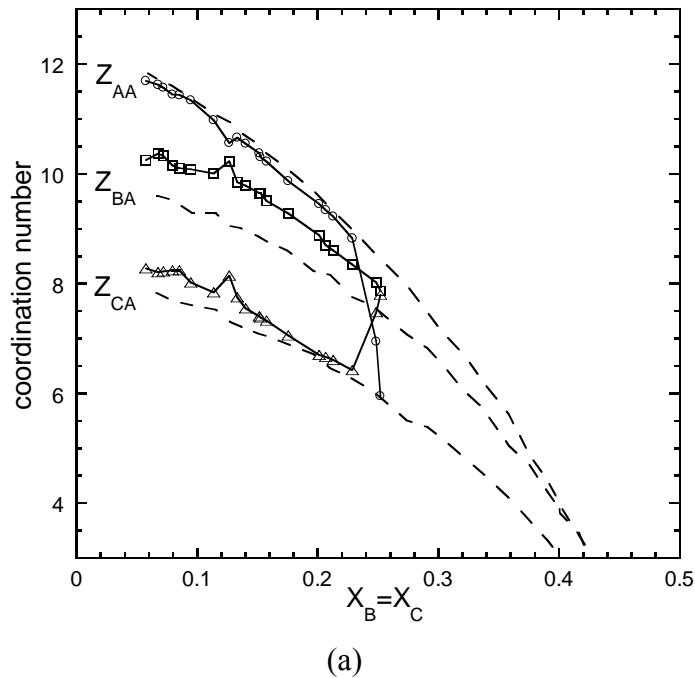
occupy NaCl positions while Cu sits on tetrahedral interstices of the fcc lattice. The AlFe_3 can be obtained out of this structure if the Mn atoms are replaced by Cu.

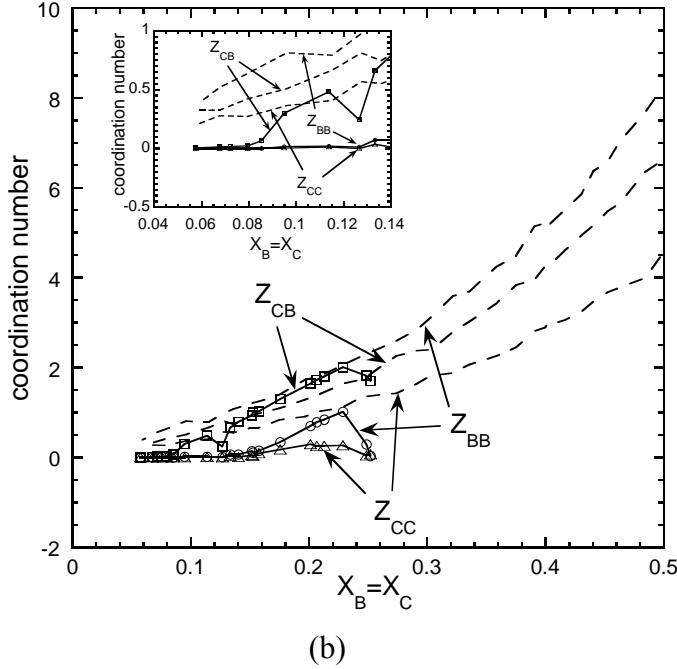
For compositions close to $X_B=0.125$, the crystal formed could not be identified with any known structure. The packing fraction η as a function of the composition $X_B=X_C$ is shown in Figure 5. It can be seen that, except for the crystal compositions, no essential difference exist between the values obtained for constrained and unconstrained systems.

The coordination numbers Z_{ij} are shown in Figure 6. Z_{AA} , Z_{BA} and Z_{CA} tend towards their theoretical values 12, 10 and 8, respectively, when the composition decreases. The behaviour of Z_{BB} , Z_{CB} and Z_{CC} with X_B is related to the NaCl lattice relaxation in the environment of A spheres. In the NaCl lattice, the distance between spheres of the same type, B-B and C-C ($\sqrt{2} a/2$), is greater than that of the B-C pair ($a/2$). Then, when the

system relaxes, two solutes of different type will have more chance to enter into contact than two solutes of the same type as the composition increases. This is reflected in the behaviour of Z_{CB} , which starts to increase from zero at $X_B=X_C\approx 0.10$, while Z_{BB} and Z_{CC} start at $X_B=X_C\approx 0.15$.

If we require that the optimal composition is again that which retains chemical ordering, then the maximum density (note that both solutes are smaller than the solvent and so the density increases with solute composition) for which all types of solute-solute contact are avoided is roughly 0.08 for each solute, or the total solute composition to be 0.16, close to the value we found for the binary system with a small solute.





(b)

Figure 6: Coordination numbers Z_{ij} for the ternary system studied, $R_B/R_A=0.80$ and $R_C/R_A=0.62$: a) Z_{AA} , Z_{BA} and Z_{CA} and b) Z_{BB} , Z_{CB} and Z_{CC} , the inset shows in more detail the behaviour in the low composition region. The full line and symbols (dashed line) correspond to the constrained (unconstrained) system.

2) Comparison of the MPA with a chemically ordered amorphous packing

The most direct test of the MPA is to compare it with the analogous amorphous structure with chemical order. We have generated such structures by starting the solutes in a random close packed structure instead of on fcc lattice sites. As described in the following section, this algorithm produces chemically ordered structures for $X_B < 0.18$. While this comparison has been complicated by the appearance of the fully crystalline states at some size ratios, we have obtained some useful results. In Table 2 we compare the value of Z_{BA} for $X_B \leq 0.2$ for the MPA and amorphous systems

R_B/R_A	$Z_{BA}(\text{MPA})$	$Z_{BA}(\text{amorphous})$
0.62	8	7.9
0.80	10	9.8

Table 2. A comparison of the values of Z_{BA} found in the MPA and a chemically ordered amorphous packing of a binary mixture of sphere with the values of R_B/R_A indicated.

These preliminary results indicate that the MPA is successfully describing important features of the local structure of the amorphous state.

3) Establishing the compositional limit on chemical order in amorphous packings of mixtures of spheres.

Starting from either the MPA or an amorphous configuration, we have identified a solute composition above which chemical order breaks down as signaled by the increase in Z_{BB} . The existence of this limiting composition is of importance in predicting the optimal composition for glass formation in an alloy. As part of this project we have formulated the following proposition:

The optimal composition for glass stability is that which produces the maximum density while a) not allowing for solute-solute contact, and b) not resulting in isolated solvents, i.e. solvents without a solute neighbour.

As shown in Figure 6, criteria a) and b) from the stability proposition coincide at a fairly well defined composition, a composition that depends on the choice of radius ratio.

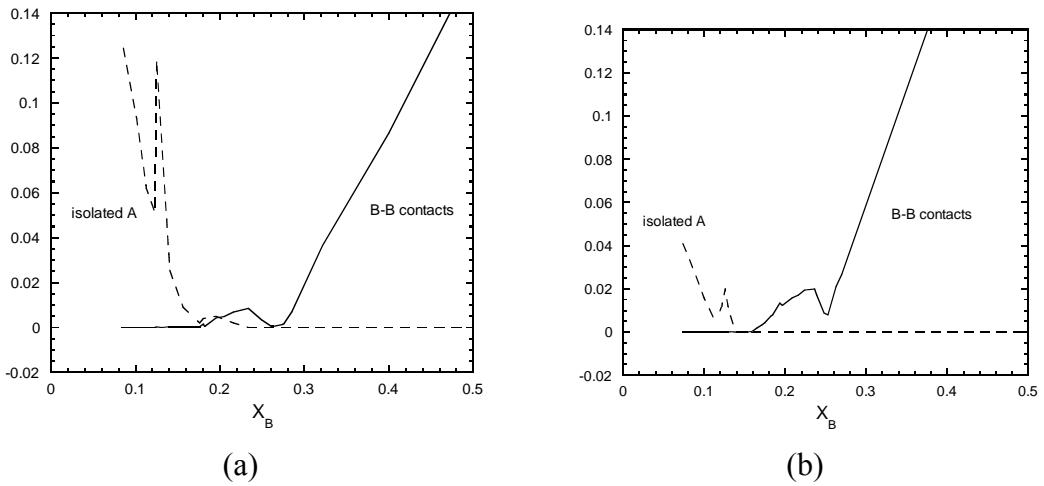


Figure 6: fraction of ‘isolated A’ spheres not having contact with any B and the fraction of ‘B-B contacts’ as a function of X_B for both system size ratios: a) $R_B/R_A=0.80$ and b) $R_B/R_A=1.12$

We have carried out a systematic study of the composition dependence of Z_{BB} in the amorphous packings, the results of which are shown in Figure 7a. In Figure 7b we plot the observed dependence of this upper compositional limit c^* on the size ratio. We find a relatively weak dependence of c^* on the size ratio with $0.14 < c^* < 0.19$ over $0.6 \leq R_B/R_A \leq 1.25$. c^* decreases steadily with increasing size of the solvent since it takes an increasing number of solvent particles per solute to keep the solutes apart.

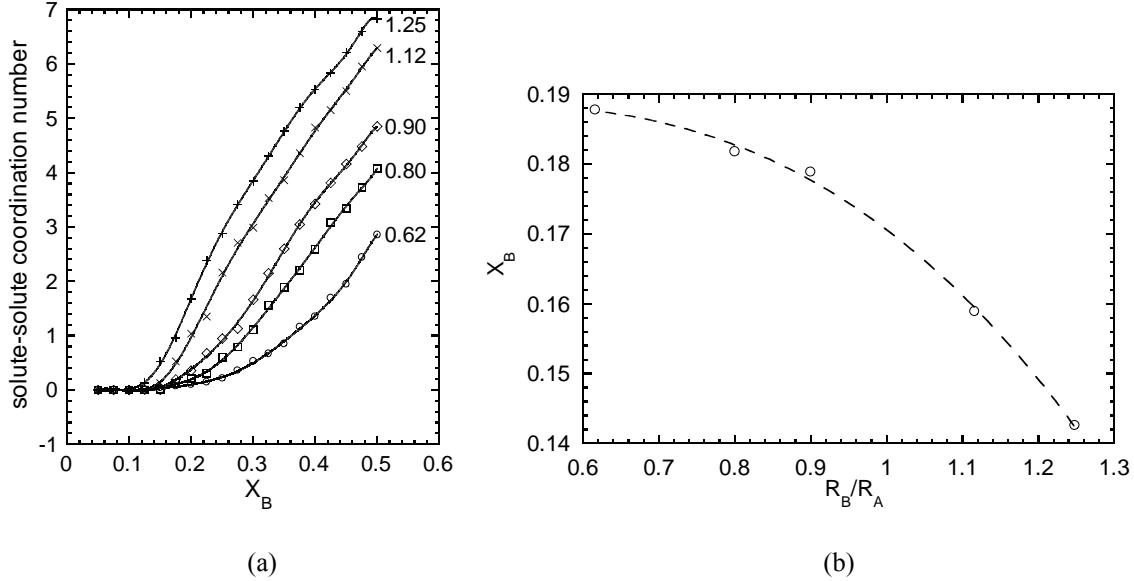


Figure 7: a) Solute-solute coordination number Z_{BB} as a function of X_B for each size ratio R_B/R_A ; b) estimated upper limit for X_B as a function of R_B/R_A (chemically ordered systems with the B spheres in random close packed positions) corresponding to a). All the lines are guides to the eye.

4) Comparison of chemically ordered amorphous sphere packing with a model metal-metalloid mixture

It is of interest to compare the coordination and structure of the constrained hard sphere mixture and a more realistic model with analogous size ratio. Here we consider a binary mixture of particles interacting by a Lennard-Jones (LJ) potential of the form

$$u_{ij}(r) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right]$$

where lengths $\sigma_{AA} = 1.0$, $\sigma_{AB} = 0.8$ and $\sigma_{BB} = 0.88$. The interaction strengths are $\epsilon_{AA} = 1.0$, $\epsilon_{AB} = 1.5$ and $\epsilon_{BB} = 0.5$ so we expect strong chemical ordering. This model has been studied extensively in the context of the glass transition and, in that field, is referred to as the KA mixture. Considering just the AA and AB lengths, this corresponds to a hard sphere size ratio of 0.6. A better approximation would involve the positions of the first peaks in g_{AA} and g_{AB} : for the quenched KA mixture it is obtained an effective size ratio of $R_B/R_A \sim 0.65$ ($r_{AA\max} \sim 1.07\sigma_{AA}$ and $r_{AB\max} \sim 0.88\sigma_{AA}$). Then, we can compare the quenched KA and the hard-sphere system with $R_B/R_A = 0.62$ (corresponding to a theoretical $Z_{BA} = 8$). We use the relationship $R_A + R_B \sim r_{AB\max}$ to scale distances from R_A units into σ_{AA} units. Again, this scaling is possible because there is almost no B-B contacts in the KA system.

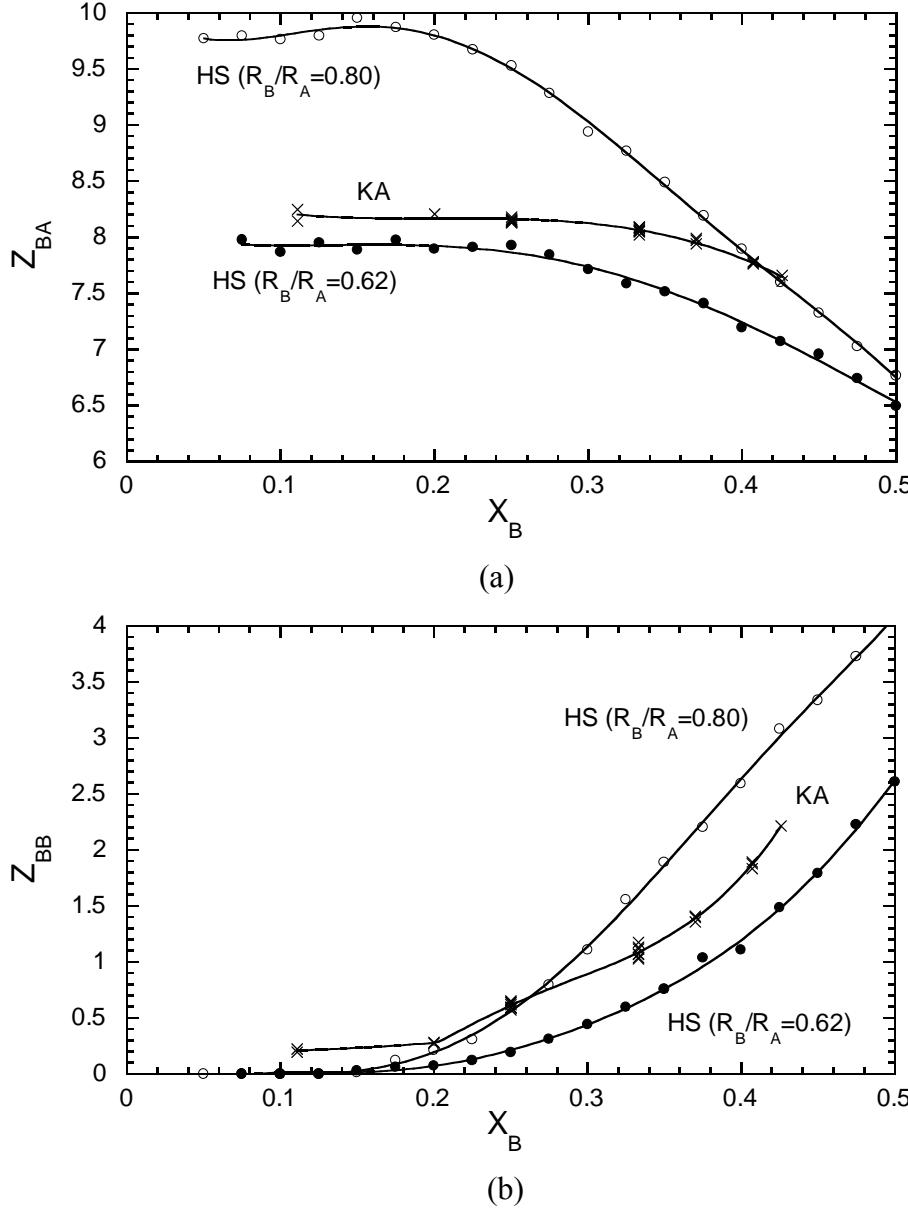


Figure 8: Average coordination numbers Z_{BA} and Z_{BB} for quenched states of the KA system ($T=0.4$) and two hard sphere mixtures with short range order ($R_B/R_A=0.62$ and 0.80) as a function of the composition X_B .

In Figure 8 we plot the coordination numbers Z_{AB} and Z_{BB} . The chemically ordered hard sphere mixture does a quite reasonable job of predicting the coordination numbers and their concentration dependence in the LJ model. We find the LJ results lie a little above the hard sphere Z_{AB} and Z_{BB} . BB contacts, explicitly excluded at low concentration in the hard sphere mixture, are present in small numbers in the unconstrained LJ system.

A sterner comparison of the two structures is provided by the radial distribution functions. In Figure 9 we compare the solute-solute distribution $g_{BB}(r)$ for the hard sphere

and LJ mixture. The LJ mixture shows considerable more well defined structure in the form of peaks at a number of distances. The HS mixture, in contrast, has a single peak (in a position similar to a peak in the LJ mixture) with broad shoulders. As demonstrated previously, the individual peaks in the LJ mixture can be assigned, unequivocally, to contributions from different types of BA^m bonds. We find that the major peak in the HS mixture and the peak at the similarly long distance in the LJ mixture arises from the BA^1 bonds (a shared vertex of the solute coordination shells). We see that missing structure in the HS mixture is due to the almost complete absence of well defined triangular face sharing (BA^3) and a very broad peak associated with the BA^2 (edge sharing) bond. The

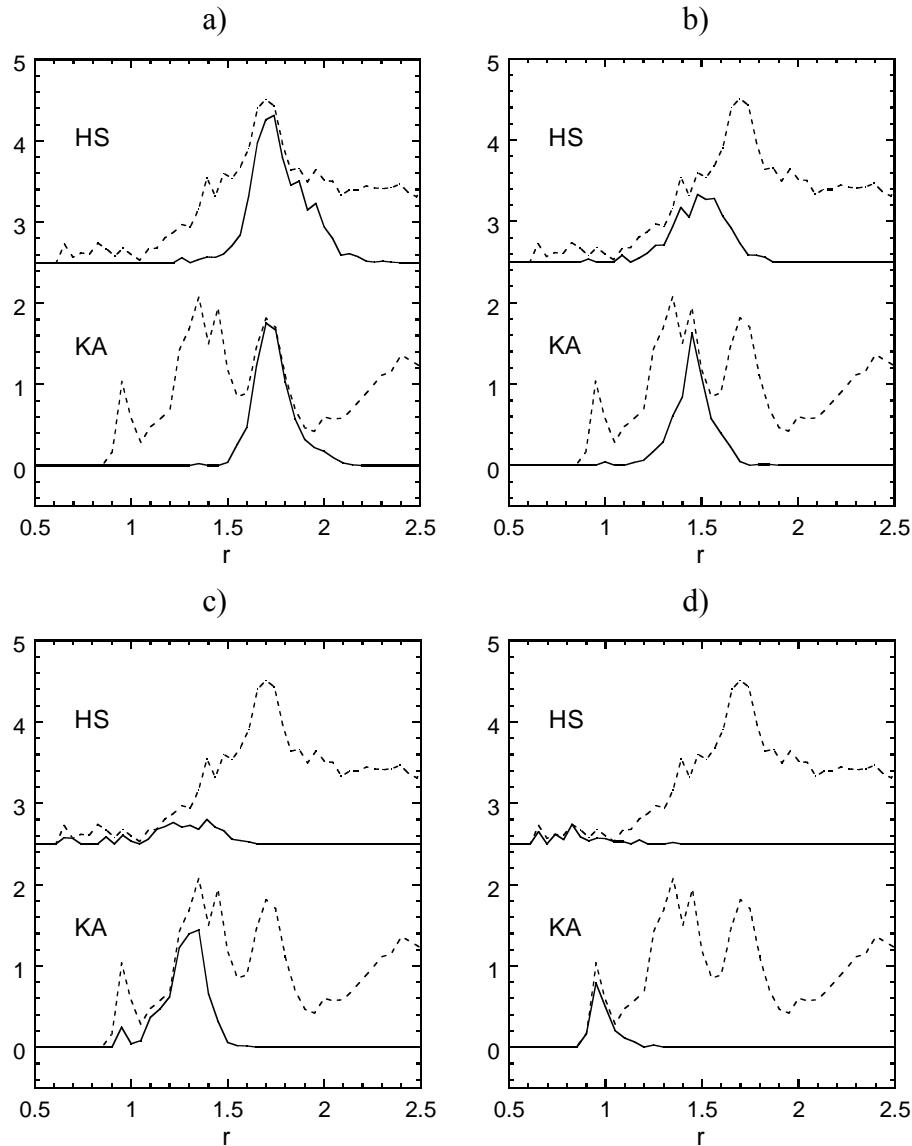


Figure 9: Partial (full line) and total (dotted line) solute-solute correlation function for hard spheres (HS) with $R_B/R_A=0.62$ and quenched KA system from $T=0.4$, both at $X_B=0.20$: a) BA^1 , b) BA^2 , c) BA^3 and d) BA^4 . The distance axis for the HS system has been scaled down by a factor 0.54 in order to change units from R_A to σ_{AA} .

impression is that the coordination shells of the solute in the HS mixture are considerably less organised than the LJ mixture. While our constraint has provided chemical order, we cannot duplicate the strong local correlations arising from the particle interactions.

5) Publications

Papers in preparation:

i) *On the Structure and Stability of a Periodic Approximate to the Structure of Amorphous Alloys.*

A.N.Alcaraz, R.S.Duhau, J. R. Fernández, P.Harrowell and D.B.Miracle

ii) *The Limiting Composition for Chemical Order in Dense Random Packings of Binary Hard Sphere Mixtures.*

A.N.Alcaraz, R.S.Duhau, J. R. Fernández, P.Harrowell and D.B.Miracle